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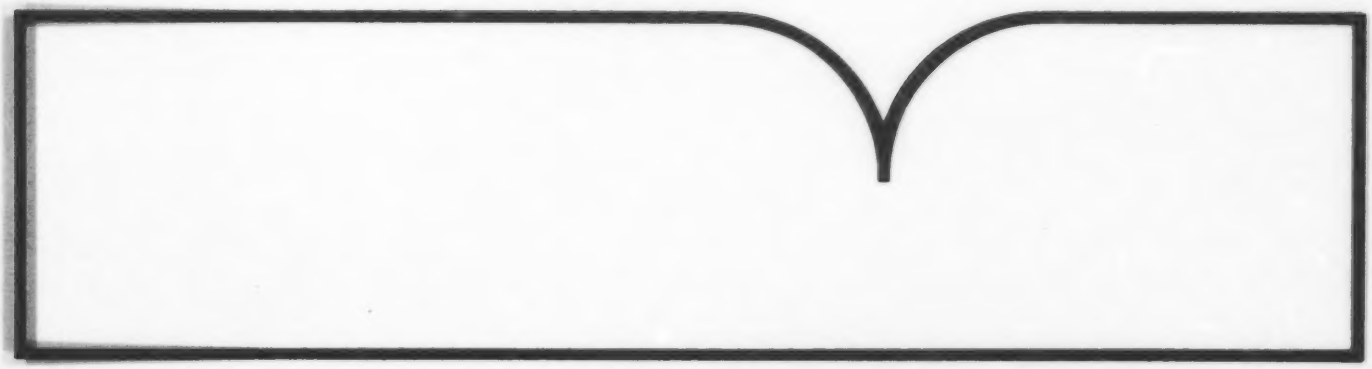

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16. ABSTRACT: The paper gives results of bench-scale reactivity studies of alkaline sorbents, performed in an integrated fixed-bed reactor, simulating the fabric filter dust layer of dry flue gas desulfurization (FGD) systems. Relative humidity significantly affected SO2 absorption by lime and limestone plus additives such as CaCl2, Ca(NO3)2, and NaNO3, but had less impact on NaHCO3 reactivity. Different reaction patterns of various sorbents were observed. Results are discussed relating to sorbent screening for dry FGD systems. (Copyright (c) Environmental Progress, 1987.)

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Alkalinity	Dry SO2 Removal	07D
Sulfur Oxides		07B
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JOURNAL ARTICLE

Evaluation of Sorbents and Additives for Dry SO_2 Removal

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Bench scale studies of the reaction between sulfur dioxide and alkaline sorbents were performed in an integrated fixed bed reactor at low temperature, simulating the fabric filter dust layer of dry FGD systems with SO_2 laden gas passing through it. Three major groups of sorbents were tested: calcitic and dolomitic hydrated lime, sodium bicarbonate, and limestone (calcite and aragonite) with salt additives such as $CaCl_2$, $Ca(NO_3)_2$, and $NaNO_3$. Relative humidity significantly affected SO_2 absorption by lime and limestone plus additives, but had less impact on $NaHCO_3$ reactivity. Different reaction patterns for various sorbents were observed: the SO_2/hydrated lime reaction rate was reduced with conversion of the sorbent, resulting in limited lime utilization, whereas the reactions between SO_2 and $NaHCO_3$ and SO_2 and $CaCO_3$ plus additives seem to proceed a constant rate, potentially leading to high sorbent utilizations. Results are discussed relating to sorbent screening for dry FGD systems.

INTRODUCTION

The increased interest in dry flue gas desulfurization (FGD) processes for removal of sulfur dioxide (SO_2) over the last 5-10 years (specifically, the perceived need for testing, evaluating, and comparing various sorbents) has spurred the development of bench-scale apparatus to study specific FGD reactions prior to actual pilot-scale testing [1-7]. Some researchers used a differential reactor for studying the reaction kinetics; others used an integral sand bed reactor for measuring the initial rate of reaction of SO_2 with sorbent. The present work also uses a sand bed reactor for studying the reaction of gaseous SO_2 with solid sorbent, similar to an alkaline dust cake on a fabric filter with SO_2-laden flue gas passing through it. Changes in gas phase and sorbent composition during the reaction are included in the present study as they are believed to play a significant role for any industrial application.

Sorbents investigated in this work included hydrated limes, sodium bicarbonate, and limestone. Various sorbent qualities, particle sizes, and sorbent additives were tested. While performance comparisons between the various sorbents are emphasized, some reaction rate controlling models for relating performance differences between the various sorbents are also proposed and discussed.

EXPERIMENTAL APPARATUS AND TESTING FEATURES

The experimental apparatus shown in Figure 1 was developed using recommendations from other research groups performing similar studies (e.g., Gary T. Rochelle's group at the University of Texas [6, 7]) and from experience gained in initial tests stressing data quality and data repeatability. The core of the experimental apparatus is the sand bed reactor where the SO_2 in the test gas reacts with the alkaline sorbent. The sand bed reactor is a vertical packed bed of approximately 1 g sorbent dispersed in (normally) 40 g inert silica sand; the entire bed is supported on a 4.5 cm diameter fritted glass plate contained in a glass cylinder. The simulated flue gas passes down through the sand bed at a face velocity of up to 6 cm/s.

The three process variables expected to influence the SO_2 capture by the sorbent are: the SO_2 concentration in the simulated flue gas, the dry bulb temperature of the gas, and the relative humidity.

In the present work, it was decided to use pure nitrogen for simulating the dry flue gas composition. Data from Rochelle indicated no effects of oxygen and carbon dioxide on SO_2 absorption in the sand bed reactor. While separate injection of SO_2 gas into the nitrogen gas stream is possible, the need for very accurate control of small gas

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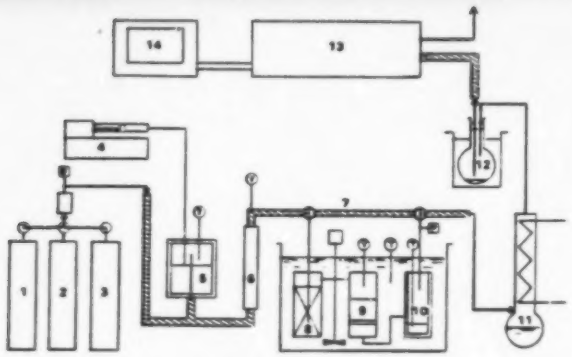

1 N_2 supply
2 Span gas
3 Test gas
4 Syringe pump
5 Evaporation chamber
6 Electrical heater
7 By-pass line
8 Back-mix chamber
9 Sand bed reactor
10 Wet bulb thermometer
11 Condenser
12 Water trap (ice)
13 SO_2 analyzer
14 Recorder

Figure 1. Experimental apparatus.

flows dictated the use of commercially available calibrated span gases of SO_2 in nitrogen (SO_2 concentration range of 500-2000 ppm) as the test gas.

The desired temperature range of 54-85°C (130-185°F) was obtained by heating the test gas prior to its entering the reactor and immersing the entire reactor vessel in a thermostated water bath.

Since a broad range of moisture content in the flue gas was needed for testing, water was continuously and accurately injected using a syringe type dispensing pump, equipped with two syringes to allow continuous operation with transient-free switchover periods. Steady evaporation was achieved using a separate hot evaporation chamber (sand reservoir heated to 150-200°C (approximately 300-400°F)) prior to mixing the vapor with the test gas. A "back-mix chamber" in the water-bath-heated section of the apparatus ensured uniformity of the gas mixture entering the sand bed reactor.

The dry bulb temperature was measured just above the sand bed reactor. The exact wet bulb temperature was measured just downstream of the reactor using a wetted wick thermometer. The difference between dry and wet bulb temperatures is the "approach to saturation," Δt_s, which together with the pressure measurement (U-tube manometer) establishes the relative humidity at test conditions. Measurement of the water injection, water collection, and gas flow rates permitted calculation of gas humidity and served as a quality control check on this important test parameter.

Prior to testing, the sand bed reactor was by-passed, and the test gas SO_2 concentration was established with a DuFont 411 SO_2 analyzer by comparison with a standard of higher SO_2 concentration (normally up to 3000 ppm). The water injection/condensation system was normally operated during the SO_2 calibration procedure. Water/SO_2 equilibrium data [8] suggest that any SO_2 capture by the condensed water would amount to less than 2-3 percent of the total amount of SO_2 in the gas phase. This was confirmed by repeated comparisons of SO_2 analyzer data using dry gas calibration followed by calibration with water injection/condensation operation. During testing, the gas passed from the sand bed reactor via the water condensation system to the SO_2 monitor, and SO_2 absorption in the sand bed reactor was established by integration of the recorded SO_2 concentration/time curve.

SAND BED REACTOR MODEL

Work by others [5] suggests that satisfactory dispersion of sorbent in the sand bed (i.e., good mixing and little agglomeration of sorbent particles) seems to be achieved when using 40 g sand per 1-2 g sorbent. The satisfactory repeatability of results obtained in the present work seems to support this assumption. The sand bed containing the alkaline sorbent is of cylindrical shape (approximately 4.5 cm in diameter and 1.6 cm in length when using 40 g sand). Supplier specification of the sand (Ottawa Industrial Sand Co., Grade F-70) and independent measurements indicate a bed voidage of $\epsilon = 0.40$. The intensity of dispersion can be estimated using the methods of Levenspiel [9] for calculation of the Reynolds, Re, and Schmidt, Sc, numbers normally used in the tests:

$$Re = \frac{d_p u \rho}{\mu} = \frac{(1.4 \times 10^{-3}) \times (6.0) \times (1.0 \times 10^{-3})}{190 \times 10^{-3}} = 0.4 \quad (1)$$

$$Sc = \frac{\mu}{\rho D_{SO_2}} = \frac{190 \times 10^{-3}}{(1.0 \times 10^{-3}) \times (0.156)} = 1.2 \quad (2)$$

where d_p = particle diameter, cm
ρ = gas density, g/cm³
u = face velocity, cm/s
μ = gas viscosity, g/cm-s
D_{SO_2} = SO_2 molecular diffusion coefficient, cm²/s

Using the chart in Reference 9 for a plug-flow fixed-bed reactor with $\epsilon = 0.40$ gives a dispersion coefficient, D, of 0.132. From the above data for the sand bed, the dispersion number becomes:

$$\frac{D}{uL} = \frac{0.132}{(6.0) \times (1.6)} = 0.014 \quad (3)$$

where L is the height of sand bed reactor in centimeters.

This low dispersion number suggests that the effects of mixed flow probably can be disregarded and that a plug flow model is a reasonable assumption.

The accepted model for this type of heterogeneous reaction is the unreacted core model in which the reaction starts at the outer skin of the particle, and the zone of reaction then moves progressively into the particle, leaving behind completely converted reaction products, or ash. Applying this model for the SO_2/sorbent reaction, the following three reaction steps are proposed, each of which potentially could control the overall rate of conversion of SO_2 with sorbent:

1. Diffusion of gaseous SO_2 to the surface of the solid particle.
2. Penetration and diffusion of SO_2 through the ash layer to the surface of the unreacted core.
3. Reaction of SO_2 with sorbent at the core reaction surface.

While the present test work does not aim to completely establish the system's reactions for different sorbents using any of the above mechanisms with related rate constants, such a model can be very helpful in interpreting and evaluating data. The difficulty in precisely determining any of the above mechanisms as the sole overall rate controlling step using data from the sand bed reactor is related to the semi-batch characteristics of the experimental apparatus (the SO_2 flow is continuous over a batch of sorbent), which increases the probability of having different mechanisms controlling the overall rate at different times.

Relative to the gas film diffusion step, the dispersion of the solid sorbent in an inert silica sand avoids both channeling and by-passing of the sorbent, enabling a uniform gas flow with well defined gas/solid contact. Assuming satisfactory dispersion of sorbent without significant agglomeration, the mass transfer number for SO_2 from the gas phase to sorbent surface can be estimated using the modified Reynolds number [8]:

$$\bar{Re} = \frac{d_p \mu \rho}{\mu (1 - \epsilon)}$$

$$= \frac{(1.4 \times 10^{-5}) \times (6.0) \times (1.0 \times 10^{-3})}{(190 \times 10^{-5}) \times (0.60)} = 0.74 \qquad (4)$$

Colburn's j-factor for mass transfer [8] is:

$$j_D = 5.7 \times (\bar{Re})^{-0.78} = 5.7 \times (0.74)^{-0.78} = 7.2 \qquad (5)$$

Using the earlier calculated Schmidt number, the gas transfer number is:

$$k_g = j_D \frac{G}{M} Sc^{-2/3} = (7.2) \frac{(0.0057)}{(28)} (1.2)^{-2/3}$$

$$= 1.3 \times 10^{-3} \text{ mol/cm}^2\text{-s} \qquad (6)$$

where G = mass gas flow, g/cm²-s
M = gas molecular weight, g/mol

A gas transfer coefficient of 1.3×10^{-3} mol/cm²-s suggests a very fast mass transfer rate from gas to solid sorbent. Using the equation from Levenspiel (9) expressing time, τ, for complete reaction of a solid particle with a gas and assuming that gas film diffusion is rate controlling:

$$\tau = \frac{\rho_B R}{3bk_g C_{As}}$$

$$= \frac{(0.03) \times (5 \times 10^{-4})}{3 \times 1 \times (1.3 \times 10^{-3}) \times (5 \times 10^{-4})} = 7.7 \text{ sec} \qquad (7)$$

where ρ_B = sorbent particle molar density, for calcium hydroxide [$Ca(OH)_2$], mol/cm³
R = sorbent particle radius, cm
b = reaction stoichiometry for $Ca(OH)_2$
C_{As} = bulk concentration of SO_2 in gas phase (for 500 ppm), mol SO_2/mol gas

This example suggests that a 10 μm diameter hydrated lime particle would react totally with SO_2 in a matter of seconds if gas-phase diffusion were the overall rate controlling step. As the measured time for reaction is much longer (as will be seen, significant amounts of unconverted sorbent are found even after 1 hr reaction), gas film diffusion can probably be excluded as the overall rate controlling step. This result also indicates that the actual gas face velocity chosen would not impact the overall rate of reaction.

EXPERIMENTS AND RESULTS

Results Using Hydrated Limes as Sorbents

As the present test work compares performance between various sorbents and the effect of changing selected process conditions, a "baseline" sorbent and some standard operating conditions were chosen: 1 g of reagent grade $Ca(OH)_2$ (Fisher C-97) dispersed in 40 g sand, the sand bed reactor operated at 64.4°C (148°F), and 325 l/h (approximately 10 scfh) nitrogen with 500 ppm SO_2 supplied to the reactor. A reference time of one hour was used for testing.

A typical SO_2 outlet concentration/time curve for a single run is shown in Figure 2. Zero outlet concentration was measured during the initial testing period, but later the SO_2 outlet concentration rises and approaches that of the inlet, indicating no further SO_2 absorption taking place in the reactor. The total amount of SO_2 absorbed during the run was found by integration of the area above the recorded curve, and comparison of the SO_2 absorbed with the amount of $Ca(OH)_2$ initially present led to the conclusion that a significant amount of $Ca(OH)_2$ (60-90 percent) had not reacted with SO_2. This result might be explained in terms of conventional theory as follows. Initially, no ash diffusion resistance exists, and all SO_2 reacts with fresh surface $Ca(OH)_2$. Ash building up on the particle surface causes the reaction rate to decrease and the sand bed outlet SO_2 concentration to rise. Eventually the reaction

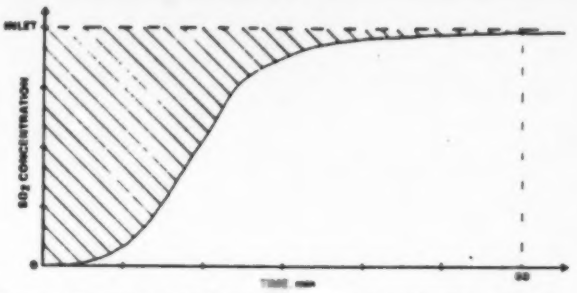

Figure 2. Generic strip chart from SO_2 analyzer using $Ca(OH)_2$ as sorbent in the sand bed.

ceases, and the SO_2 outlet concentration equals the inlet concentration, which corresponds to the ash diffusion resistance having reached an extremely high value. "Blinding" of the sorbent surface is probably a better description of this phenomenon.

Figure 3 depicts the amount of sorbent converted with SO_2 (mol SO_2/mol $Ca(OH)_2$ present) after one hour for different relative humidities. Although no definite proof can be given at this point, it seems that the ash diffusion resistance, being the most probable mechanism stopping the reaction ("blinding"), is strongly related to relative humidity in the gas phase, probably via water adsorption on the particle. An important implication of this "blinding" of the sorbent surface is that the total conversion cannot be in-

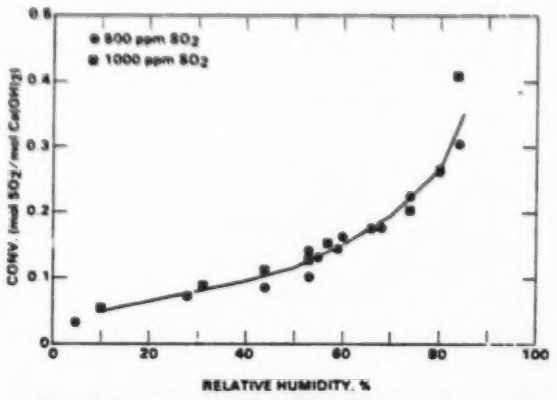

Figure 3. Conversion of reagent grade $Ca(OH)_2$ with SO_2 (1 hour) 1 g $Ca(OH)_2$, 64.4°C (148°F).

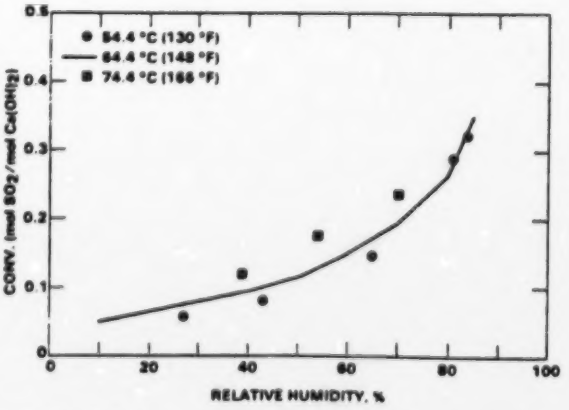

Figure 4. Conversion of reagent grade $Ca(OH)_2$ with SO_2 (1 hour) 1 g $Ca(OH)_2$, 500 ppm SO_2.

creased by increasing the SO_2 partial pressure in the gas phase. This was confirmed by tests using 1000 ppm SO_2 as shown in Figure 3.

Figure 4 shows the effect of temperature on SO_2 absorption. It appears that the conversion of $Ca(OH)_2$ with SO_2 increases somewhat with temperature for constant relative humidity, the order of magnitude is 20-30 percent per 10°C (18°F).

Some commercially available pressure hydrated limes have also been tested in the sand bed reactor. The results, shown in Figure 5, revealed somewhat lower SO_2 absorption by these hydrates in the range from 50 percent relative humidity, Δt_s = 13°C (24°F), to 70 percent relative humidity, Δt_s = 7°C (12°F), than by reagent grade $Ca(OH)_2$. Using the BET surface area to compare results achieved in the sand bed reactor, a correlation between surface area and SO_2 absorption can be seen for the dolomitic samples, but none is apparent for the few calcitic types, based on these data.

Some inorganic salts were also tested as additives to reagent grade $Ca(OH)_2$: calcium chloride ($CaCl_2$), sodium chloride (NaCl), sodium hydroxide (NaOH), and sodium nitrate ($NaNO_3$). The results of these tests are depicted in Figure 6. Each was mixed with $Ca(OH)_2$ in a dry procedure, and not by the procedure of water dissolution and mixing with sorbent followed by drying, as done by others [6, 7]. The outlet SO_2 concentration/time curves were similar to those described above for pure $Ca(OH)_2$, but all additives shifted the ultimate SO_2 absorption somewhat. Continuing what was said earlier, this would indicate that the additive changes the ultimately controlling SO_2 ash "blinding" effect correspondingly. The most notable result is probably the quite significant increase in SO_2 absorption using $CaCl_2$ as additive. Relating to an earlier statement regarding water adsorption on the lime particles, it is believed that the $CaCl_2$, having a high water affinity ("hygroscopic salt"), increases the water absorbed by the particle, thereby reducing the SO_2 ash "blinding" effect.

Results Using Sodium Compounds as Sorbents

Most bench-scale studies using sodium compounds as dry sorbents for SO_2 removal have been performed at temperatures in the range 150-250°C (300-500°F) [1]. Sodium bicarbonate, $NaHCO_3$, which has been extensively studied, thermally decomposes to anhydrous soda ash at these temperatures, which has often been claimed to be an important factor in the SO_2 removal process. The present work, however, focuses on the reactions at a lower temperature, 64.4°C (148°F), where the effect of thermal decomposition of $NaHCO_3$ is expected to be less significant. To investigate thermal decomposition effects, some comparison tests were done using different time periods for "conditioning" sorbent samples (at test conditions of temperature and humidity) prior to exposure to the SO_2 test gas. Subsequent testing, however, gave the same SO_2 absorption results, independent of differences in time periods of "conditioning."

A typical SO_2 concentration/time curve as recorded by the SO_2 monitor using reagent grade (Fisher S-233) $NaHCO_3$ as sorbent in the sand bed reactor is shown in Figure 7. It appears that a steady SO_2 removal rate is established within a few minutes of sorbent exposure to SO_2. This nearly constant rate, or constant SO_2 removal efficiency, is maintained throughout the testing period, being reduced only slightly with the gradual consumption of sorbent. This is entirely different from what was observed above using $Ca(OH)_2$ as sorbent (Figure 2).

A series of tests at different relative humidities showed somewhat increased SO_2 absorption with increased humidity. Also, tests were made using different amounts of $NaHCO_3$ in the sand bed and different SO_2 concentration levels. To help interpret these results, a plug flow reactor model was adopted for which the performance equation is [9]:

$$\tau = C_{SO_2}^{\circ} \int_0^{X_{SO_2}} \frac{dX_{SO_2}}{-r_{SO_2}} \qquad (8)$$

where τ = space time = $\frac{V\epsilon}{v_o}$, h

V = sand bed volume, ml

ϵ = sand bed voidage, fraction

v_o = gas volumetric flow, ml/h

$-r_{SO_2}$ = rate of disappearance of SO_2 = $\frac{-dC_{SO_2}}{dt}$, mol/l-h

$C_{SO_2}^{\circ}$ = inlet SO_2 concentration, mol/l

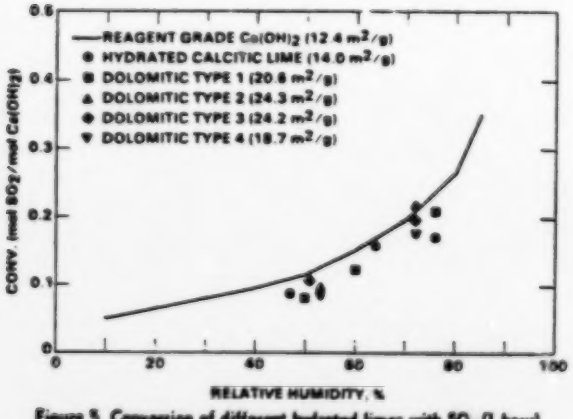
REAGENT GRADE Ca(OH)2 (12.4 m2/g)
HYDRATED CALCITIC LIME (14.0 m2/g)
DOLOMITIC TYPE 1 (20.8 m2/g)
DOLOMITIC TYPE 2 (24.3 m2/g)
DOLOMITIC TYPE 3 (24.2 m2/g)
DOLOMITIC TYPE 4 (18.7 m2/g)
CONV. (mol SO2/mol Ca(OH)2)
RELATIVE HUMIDITY, %

Figure 5. Conversion of different hydrated limes with SO_2 (1 hour) 1 g sorbent, 64.4°C (148°F), 500 ppm SO_2.

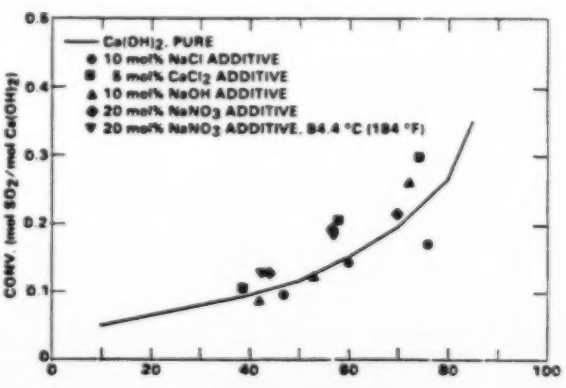
Ca(OH)2, PURE
10 mol% NaCl ADDITIVE
5 mol% CaCl2 ADDITIVE
10 mol% NaOH ADDITIVE
20 mol% NaNO3 ADDITIVE
20 mol% NaNO3 ADDITIVE, 84.4 °C (184 °F)
CONV. (mol SO2/mol Ca(OH)2)
RELATIVE HUMIDITY, %

Figure 6. Conversion of $Ca(OH)_2$ + additives with SO_2 (1 hour) 1 g $Ca(OH)_2$, 64.4°C (148°F), 500 ppm SO_2.

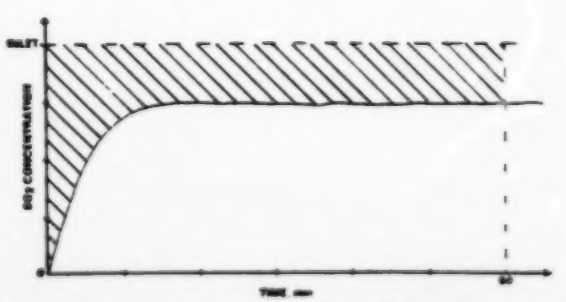

Figure 7. Generic strip chart from SO_2 analyzer using $NaHCO_3$ (or $CaCO_3$ + additive) as sorbent in the sand bed.

X_{SO_2} = conversion of SO_2, fraction
$X_{SO_2 f}$ = outlet conversion of SO_2, fraction

If the reaction rate is expressed as a first order reaction in both sorbent and SO_2, then:

$$-r_{SO_2} = kC_{sorb}C_{SO_2} = k\frac{N_{sorb}}{V(1-\epsilon)}C_{SO_2}^{\circ}(1 - X_{SO_2}) \quad (9)$$

where k = a rate constant for the reaction, l/mol-h
C_{sorb} = concentration of sorbent in the sand bed, mol/l
N_{sorb} = amount of sorbent in the sand bed, mmol

As the total amount of sorbent is fairly large, compared to the amount reacted during the reaction period of interest, assume:

$$N_{sorb} = N_{sorb}^{\circ} \text{ (initial amount of sorbent)}$$

Inserting these expressions in the performance equation (Equation 8) and expressing the sorbent as sodium oxide, Na_2O, yields:

$$\tau = \frac{V\epsilon}{v_o} = \frac{V(1-\epsilon)}{kN_{Na_2}^{\circ}o}\int_0^{X_{SO_2 f}}\frac{dX_{SO_2}}{1 - X_{SO_2}}$$

$$= \frac{V(1-\epsilon)}{k\,N_{Na_2}^{\circ}o}(-\ln(1 - X_{SO_2 f})) \quad (10)$$

Rearranging,

$$-\ln(1 - X_{SO_2 f}) = k\frac{\epsilon}{v_o(1-\epsilon)}N_{Na_2}^{\circ}o \quad (11)$$

The left side of Equation 11 has been plotted versus $N_{Na_2}^{\circ}o$ for all test runs using $NaHCO_3$ as the sorbent and is depicted in Figure 8. In the low humidity range, the slopes of the linear curves indicate the rate constant, k, of 8, 18, and 25 × 10^2 l/mol-h almost proportional to the corresponding relative humidities of 15, 30-35, and 45-50 percent, respectively. For higher relative humidity, 70-75 percent, interpretation of the results seems more complex in terms of the above equation; the plot reveals the same straight line slope as was observed at 50 percent relative humidity. Even at the quite high SO_2 absorption rates (at high humidity, the measured range covers 40-75 percent steady state SO_2 removal across the sand bed reactor), however, no reaction inhibiting effects such as "blinding" were seen. A probable mechanism could be the CO_2 released during reaction with SO_2 creating sufficient fresh surface of sorbent to account for the continued reaction.

A few test runs were also made using reagent grade anhydrous sodium carbonate, Na_2CO_3, (Fisher S-263) as sorbent. However, very low SO_2 absorption (less than 5 percent of that seen when using $NaHCO_3$), even at high relative humidity, was observed in the sand bed reactor, and no steady removal rate could be detected. Based on these data, it seems that the above reported fast reaction between SO_2 and $NaHCO_3$ at 64.4°C (148°F) proceeds without any intermediately formed anhydrous Na_2CO_3.

Figure 9 depicts the SO_2 absorption achieved in the sand bed, expressed as conversion of Na_2O, after one hour, as a function of the relative humidity using various $NaHCO_3$ samples as sorbents. The difference in results between the various samples of $NaHCO_3$ is noteworthy, and is probably related to differences in surface area or other particle characteristics. However, a measurable quantity identifying these differences seems needed.

In summary, the relative humidity is less critical to SO_2 absorption by $NaHCO_3$ at low temperature than is $Ca(OH)_2$. The reaction seems to be first order with respect to both SO_2 and sorbent. Based on what has been observed here, a mechanism involving the release of CO_2 during the reaction of SO_2 with $NaHCO_3$ seems best to explain the high reactivity of $NaHCO_3$ without any "blinding" effects.

Results Using Calcium Carbonate as Sorbent

Tests using pure reagent grade calcium carbonate, $CaCO_3$, (Fischer C-64) and gas relative humidities in the range 40-70 percent (Δt_s approx. 17-7°C (30-12°F)) revealed no SO_2 absorption in the sand bed reactor. SO_2 absorption by limestone under dry conditions has been reported by others to be enhanced by use of deliquescent salt additives, specifically $CaCl_2$ [5, 6]. The additive enhancement of the sorbent has usually been done by mixing the sorbent with an aqueous solution of the additive followed by drying of the mixture. In the present work, however, the sorbent and additive were mixed dry to exclude any effect of specific sorbent pretreatment on the results obtained in the sand bed reactor.

The additive $CaCl_2 \cdot 2H_2O$ was mixed with the sorbent $CaCO_3$ in the amounts of 0.1 and 0.2 g, respectively, per 1 g sorbent. The effect of the additive on the SO_2 absorption measured in the sand bed was significant. Adding $CaCl_2 \cdot 2H_2O$ to $CaCO_3$ in the amount of 0.1 g/g (approximately 7 mol percent) resulted in the definite reaction of SO_2 with $CaCO_3$ at 70 percent relative humidity (about 0.1 mol SO_2/mol $CaCO_3$ after one hour); however, using 0.2 g/g (approximately 13.5 mol percent) resulted in a SO_2 absorption at a magnitude similar to that observed earlier using pure reagent grade $Ca(OH)_2$ at the same conditions (about 0.2 mol SO_2/mol $CaCO_3$ after one hour). These results become even more noteworthy as the reaction of SO_2 with $CaCO_3$ gave a constant SO_2 removal efficiency across the sand bed throughout the testing period, similar to that described above using $NaHCO_3$ as sorbent (Figure 7), but different from that seen with $Ca(OH)_2$ (Figure 2). These observations indicate that the significant reaction inhibiting effect with sorbent conversion ("blinding") which

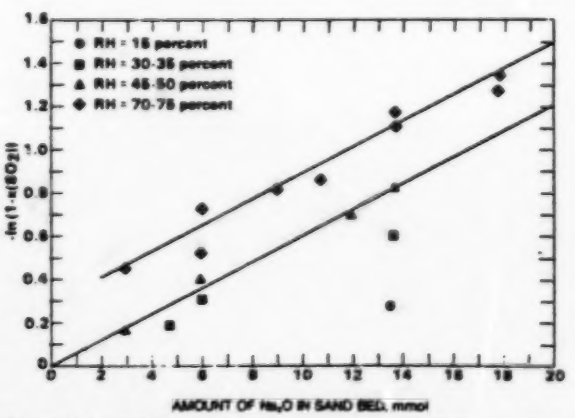

Figure 8. Logarithmic plot of SO_2 removal using $NaHCO_3$ as sorbent 64.4°C (148°F), 500-1000 ppm SO_2.

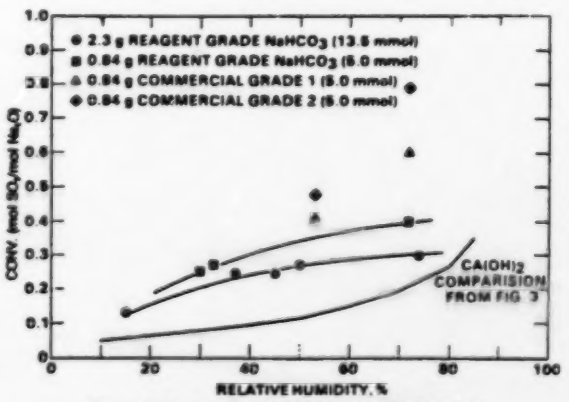
2.3 g REAGENT GRADE NaHCO3 (13.6 mmol)
0.84 g REAGENT GRADE NaHCO3 (5.0 mmol)
0.84 g COMMERCIAL GRADE 1 (5.0 mmol)
0.84 g COMMERCIAL GRADE 2 (5.0 mmol)
CONV. (mol SO2/mol Na2O)
Ca(OH)2 COMPARISION FROM FIG. 3
RELATIVE HUMIDITY, %

Figure 9. Conversion of $NaHCO_3$ with SO_2 (1 hour) 64.4°C (148°F), 500 ppm SO_2.

was assessed earlier using $Ca(OH)_2$ as sorbent, does not seem to exist using $CaCl_2$-enhanced limestone. The reaction is constantly proceeding, its rate decreasing only with the depletion of $CaCO_3$ sorbent.

A test matrix using 0.2 g $CaCl_2 \cdot 2H_2O$ per 1 g $CaCO_3$ and 70 percent relative humidity of 64.4°C (148°F) was performed with varying inlet SO_2 concentration, amount of $CaCO_3$ sorbent, and amount of sand as test parameters. The results, depicted in Figure 10, suggested that:

1. SO_2 absorption increases proportionally with the amount of sorbent.
2. SO_2 absorption increases with the SO_2 concentration up to approximately 1000 ppm for most conditions tested.
3. The amount of sand used in the bed does not have any significant impact on the amount of SO_2 absorbed. (Only at the conditions where the SO_2 concentration and sorbent amount were at their maximums might an impact of the total quantity of sand also be detectable.)

These results do not support a single mechanism as rate controlling for SO_2 removal at the different test conditions.

Relative humidity is very critical to the degree of SO_2 removal which is achievable (also explaining some scatter observed in the above results). Lowering the relative humidity from 70 percent (Δt, approximately 7°C (12°F)) to 50 percent (Δt, approximately 13°C (24°F)) stops virtually all reaction of SO_2 with $CaCO_3$. Raising the dry bulb temperature from 64.4°C (148°F) to 74.4°C (166°F) also rapidly decreases the SO_2 removal, corresponding to lowering the relative humidity from 70 to 50 percent. Only by raising the wet bulb temperature correspondingly to restore the relative humidity could high SO_2 absorption be maintained (Figure 11).

In summary, the theory of a deliquescent salt, $CaCl_2$, generating a liquid phase for SO_2 reaction with $CaCO_3$ [5] agrees well with test results noted here. These results imply that a steady state SO_2 removal rate can be maintained across the sand bed reactor, unlike the reaction of SO_2 with $Ca(OH)_2$ where the reaction rate decreased with time ("blinding").

A few tests performed using NaCl instead of $CaCl_2$ as an additive to limestone revealed no reaction between SO_2 and $CaCO_3$. In terms of the above conclusion, this would indicate that the less hygroscopic NaCl (i.e., less affinity for water) does not generate sufficient liquid phase on the particle surface for the dissolution and reaction of $CaCO_3$ with SO_2.

Several commercial limestones [Fredonia (Kentucky) and aragonite] have been tested with $CaCl_2$ as the additive and samples of two different particle sizes (all particles minus 325 mesh or all particles in the range

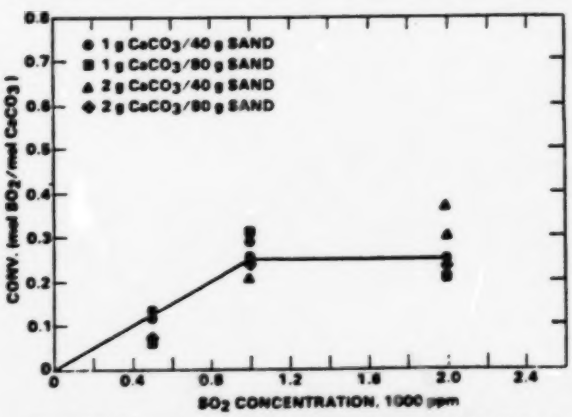

Figure 10. Conversion of chloride enhanced $CaCO_3$ with SO_2 (1 hour)
0.2 g ($CaCl_2 \cdot 2H_2O$)/g $CaCO_3$
64.4°C (148°F), RH = 70 percent.

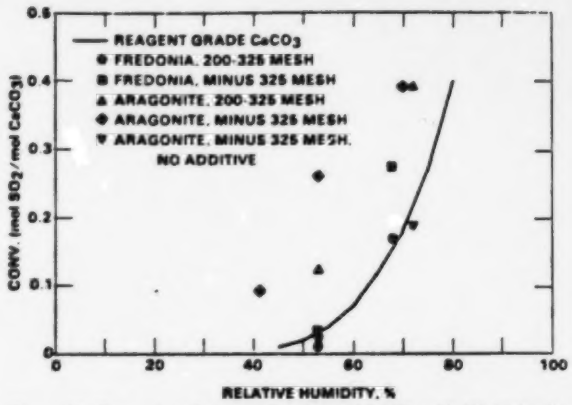

Figure 11. Conversion of various Cl enhanced $CaCO_3$ with SO_2 (1 hour)
2 g $CaCO_3$, 0.2 g ($CaCl_2 \cdot 2H_2O$)/g $CaCO_3$
64.4°C (148°F), 1000 ppm SO_2.

200-325 mesh). The results shown in Figure 11 portray the minus 325 mesh sample of Fredonia (a calcite) to react somewhat faster with SO_2 at 70 percent relative humidity than did reagent grade $CaCO_3$. This might be attributed to the higher specific surface area of the finer particles. For aragonite a significantly higher SO_2 absorption rate occurred than for either of the tested calcites: the difference was probably related to the different crystal structure or surface shape. Significant SO_2 was also removed with argonite at lower relative humidity (40-50 percent relative humidity, Δt, approximately 17-12°C (30-22°F)), especially with the fine particulate fraction (minus 325 mesh) sample of sorbent. Results of a few tests using aragonite without additive enhancement are also presented in Figure 11. Clearly, some SO_2 absorption was achieved at high relative humidity, which seems to confirm that the specific sorbent crystal or surface characteristics might be as important for high SO_2 removal as the increased liquid phase obtained by addition of a deliquescent salt.

The last test series to be reported here used sodium nitrate, $NaNO_3$, and calcium nitrate, $Ca(NO_3)_2$, as additives to reagent grade $CaCO_3$ sorbent, and also revealed quite high SO_2 absorption in the sand bed when operating at high relative humidity (70 percent relative humidity, Δt, approximately 7°C (12°F)). Moreover, use of both additives revealed a constant SO_2 removal across the sand bed throughout the testing period, similar to that described above for $CaCl_2$ added to $CaCO_3$. A "blank" test using only $NaNO_3$ in the sand bed showed no absorption of SO_2 at similar conditions, suggesting that only a reaction between SO_2 and $CaCO_3$, enhanced by the nitrate compound, could explain the results. The results of a small test matrix aimed at evaluating the effects of the amount of additive used and the SO_2 concentration are shown in Figure 12. Surprisingly, these results showed that, for given test conditions, there seems to be an optimum ratio of additive to sorbent for maximum absorption of SO_2 by $CaCO_3$. Recalling the previous discussion of a liquid phase on the particle surface, this indicates that a specific ratio of SO_2 to NO_3^- in the liquid phase results in the highest dissolution rate for $CaCO_3$. While this effect cannot be explained at this point, it is noted that a similar "SO_x/NO_x ratio" has been reported to play a role for simultaneous SO_x/NO_x removal in a spray dryer/baghouse process [*10*].

The SO_2 conversion achieved in the sand bed in tests using nitrate additives could show some effect of the time used for "conditioning" the sorbent sample. Also, an increasing SO_2 removal efficiency across the sand bed during the testing period could sometimes be observed. These observations suggest that a time factor related to achievement of equilibrium for this specific system might

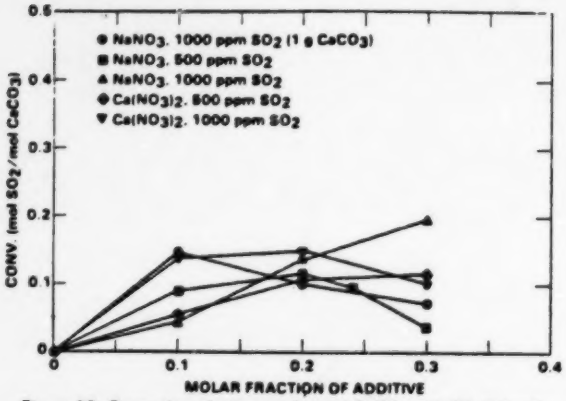

Figure 12. Conversion of nitrate enhanced $CaCO_3$ with SO_2 (1 hour) 2 g $CaCO_3$, 64.4°C (148°F), RH = 70 percent.

be of importance for the reaction performance.

Finally, some tests with relative humidity and dry bulb temperature as parameters for the $CaCO_3$/nitrate system were also made, but the results were similar to those observed with $CaCl_2$ added to $CaCO_3$. Thus, the relative humidity (or approach to saturation), not the actual temperature, seems to control the SO_2 absorbed in the sand bed.

CONCLUSIONS

- The sand bed reactor has been developed as a useful tool for studying dry sorbent reactions with SO_2 at low temperatures.
- Hydrated limes react with SO_2 in the temperature range 55-75°C (130-166°F) with the conversion increasing markedly with the gas relative humidity. This agrees with pilot and full-scale dry scrubber test work showing SO_2 removal to increase with decreasing approach to saturation.
- At some conditions the lime conversion can be increased 20-30 percent by using 5-10 mol percent salt additives.
- The SO_2/lime reaction is inhibited with conversion of the sorbent, probably due to ash buildup on the particle surface ("blinding"). The implication is that a process using recycle of lime sorbent would require some "reactivation" to remove this ash layer to achieve high lime utilization.
- Sodium bicarbonate efficiently absorbs SO_2 at 65°C (148°F), but the absorption increases less with increasing gas relative humidity than seen with $Ca(OH)_2$ sorbent. This indicates that a soda based dry scrubber would be less sensitive to changes in approach to saturation.
- The reaction between SO_2 and $NaHCO_3$ proceeds without any "blinding." This suggests that very high sorbent utilization can be achieved on a soda based dry scrubber by increasing sorbent residence time in the gas stream.
- Normal $CaCO_3$ does not react with SO_2 in the sand bed reactor, but the use of additives such as $CaCl_2$, $NaNO_3$, and $Ca(NO_3)_2$ significantly enhances the reaction at high relative humidity.
- Higher SO_2 absorption can be achieved using fine particulate $CaCO_3$ as sorbent and by using aragonite instead of calcite.
- The reactions of SO_2 with additive enhanced $CaCO_3$ do not indicate any "blinding" of sorbent with conversion.
- These results suggest that $CaCO_3$ with additive can be used in lieu of hydrated lime in a dry scrubbing system when operating with a low approach to saturation. Increased residence time of sorbent in the fabric filter using dry recycle of sorbent or extending time intervals between cleaning cycles can be expected to lead to higher sorbent utilization.

LITERATURE CITED

1. Davis, W. T. and T. C. Keener: "Chemical Kinetic Studies on Dry Sorbents," DOE/FC/10184-1 (DE82012765) (1982).
2. Klingspor, J., A. Stromberg, H. T. Karlsson, and I. Bjerle: "Similarities Between Lime and Limestone in Wet-Dry Scrubbing," Licentiate Thesis, University of Lund, Sweden (1983).
3. Bjerle, I., J. Klingspor, and H. T. Karlsson: "Sulfur Capture by Promoted Limestone," Presented at the 11th Annual Stack Gas Meeting, Paducah, Kentucky (October 1983).
4. Klingspor, J., H. T. Karlsson, and I. Bjerle: "A Kinetic Study of the Dry SO_2-Limestone Reaction at Low Temperature," *Chem. Eng. Commun.*, 22, 81-103 (1983).
5. Karlsson, H. T., J. Klingspor, M. Linne, and I. Bjerle, "Activated Wet-Dry Scrubbing of SO_2," *APCA Journal*, 33, (1), 23-28 (1983).
6. Ruiz-Alsop, R. N. and G. T. Rochelle: "Effect of Deliquescent Salt Additives on the Reaction of Sulfur Dioxide with Dry $Ca(OH)_2$," Preprint of paper presented at 189th ACS National Meeting, 88-97 (1985).
7. Ruiz-Alsop, R. N.: "Reaction of SO_2 with $Ca(OH)_2$," Proposal for Ph.D. Dissertation, Department of Chemical Engineering, The University of Texas at Austin (February 1984).
8. Perry and Chilton: "Chemical Engineers Handbook," Fifth Edition, McGraw-Hill (1973).
9. Levinspiel, O.: "Chemical Reaction Engineering," Second Edition, Wiley (1972).
10. Felsvang, K., P. Morsing, and P. Veltman: "Acid Rain Prevention Thru New SO_x/NO_x Dry Scrubbing Process," in *Proceedings: Eighth Symposium on Flue Gas Desulfurization*, New Orleans, LA, November 1983, Volume 2, EPA-600/9-84-017b (NTIS PB84-223049), pp. 650-667 (July 1984).

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